

Article

# A Paper-Based Microfluidic Fuel Cell Using Soft Drinks as a Renewable Energy Source

Jaime Hernández Rivera <sup>1,2</sup>, David Ortega Díaz <sup>3</sup>, Diana María Amaya Cruz <sup>4</sup>, Juvenal Rodríguez-Reséndiz <sup>5,\*</sup>, Juan Manuel Olivares Ramírez <sup>2,\*</sup>, Andrés Dector <sup>6,\*</sup>, Diana Dector <sup>1</sup>, Rosario Galindo <sup>7</sup>, and Hilda Esperanza Esparza Ponce <sup>1</sup>

- <sup>1</sup> Centro de Investigación en Materiales Avanzados, Chihuahua 31136, Mexico; jhernandezr@utsjr.edu.mx (J.H.R.); diana.dector@cimav.edu.mx (D.D.); hilda.esparza@cimav.edu.mx (H.E.E.P.)
- <sup>2</sup> Renewable Energy Department, Universidad Tecnológica de San Juan del Río, Querétaro 76800, Mexico
- <sup>3</sup> Instituto Tecnológico de San Juan del Río, Querétaro 76800, Mexico; ortegadiaz15@gmail.com
- <sup>4</sup> Facultad de Ingeniería, Universidad Autónoma de Querétaro, Campus Amealco, Querétaro 76010, Mexico; diana.amaya@uaq.mx
- <sup>5</sup> Facultad de Ingeniería, Universidad Autónoma de Querétaro, Querétaro 76010, Mexico
- <sup>6</sup> Renewable Energy Department, CONACYT–Universidad Tecnológica de San Juan del Río, Querétaro 76800, Mexico
- <sup>7</sup> CONACYT–División de Ciencias Naturales y Exactas, Universidad de Guanajuato, Guanajuato 36050, Mexico; mr.galindo@ugto.mx
- \* Correspondence: juvenal@uaq.edu.mx (J.R.-R.); jmolivaresr@utsjr.edu.mx (J.M.O.R.); adector@conacyt.mx (A.D.); Tel.: +52-427-122-4463 (J.M.O.R.)

Received: 9 April 2020; Accepted: 11 May 2020; Published: 13 May 2020



**Abstract:** The research aims were to construct an air-breathing paper-based microfluidic fuel cell (paper-based  $\mu$ FC) and to evaluated it with different soft drinks to provide energy for their prospective use in portable devices as an emergency power source. First, in a half-cell configuration, cyclic voltammetry showed that glucose, maltose, and fructose had specific oxidation zones in the presence of platinum-ruthenium on carbon (PtRu/C) when they were individual. Still, when they were mixed, glucose was observed to be oxidized to a greater extent than fructose and maltose. After, when a paper-based  $\mu$ FC was constructed, PtRu/C and platinum on carbon (Pt/C) were used as anode and cathode, the performance of this  $\mu$ FC was mostly influenced by the concentration of glucose present in each soft drink, obtaining maximum power densities at room temperature of 0.061, 0.063, 0.060, and 0.073 mW cm<sup>-2</sup> for Coca Cola<sup>®</sup>, Pepsi<sup>®</sup>, Dr. Pepper<sup>®</sup>, and 7up<sup>®</sup>, respectively. Interestingly, when the soft drinks were cooled, the performance was increased up to 85%. Furthermore, a four-cell stack  $\mu$ FC was constructed to demonstrate its usefulness as a possible power supply, obtaining a power density of 0.4 mW cm<sup>-2</sup>, using Coca Cola<sup>®</sup> as fuel and air as oxidant. Together, the results of the present study indicate an alternative application of an  $\mu$ FC using soft drinks as a backup source of energy in emergencies.

Keywords: fuel cell application; microfluidic fuel cell; power supply; soft drinks

## 1. Introduction

Actually, the performance of low-consumption electronic devices such as wireless sensors, digital clocks, and small medical devices, among others, is limited, due to the use a rechargeable lithium-ion battery [1]. In this way, the intensive research to obtain small energy sources as a possible application for low-consumption electronic devices has been directed to the use of micro fuel cells [2–6].

The paper based microfluidic fuel cells (paper based  $\mu$ FC) have been proposed as an external power source for low-consumption electronic devices [7–9]. The paper-based  $\mu$ FCs have the following advantages:

- The paper used in the paper-based µFCs construction is a very low-cost material, and consequently, the fuel cells are disposable.
- Due to the movement of reactants through capillary action, the use of external pumps is unnecessary [7].
- The ion transport is carried out through the electrolyte contained in the reactants, and as a consequence, the use of a proton or anion exchange membrane is unnecessary [10].
- These paper-based μFCs may use different liquid organic compounds as fuel, being reported to date ethanol [11], methanol [7,11], formate[12], urea [13,14], and glucose [8,15].

Research into paper-based  $\mu$ FCs using glucose as fuel has experienced a growing interest in the past few years and showing potential in electricity generation for portable devices [8,15,16]. The main advantages of using glucose had been non-toxicity and handling since it had been obtained from reactive grade glucose to body fluids such as human blood [9,17]. The above assumes that the use of other economic sources of glucose that does not require a previous treatment would constitute a significant achievement. In this context, soft drinks are an excellent alternative, since they are a cheap and highly available source; in addition, they contain other saccharides such as fructose, galactose, sucrose, lactose, and maltose, which could be used as fuel in a paper-based  $\mu$ FC.

Some relevant works evaluating paper-based  $\mu$ FCs under soft drinks are listed in the following lines:

The first research has evaluated different kinds of soft drinks (iced red tea, vegetable juice, fruit juice, and aerated water) in a miniature biofuel cell using glucose dehydrogenase and bilirubin oxidase as anode and cathode, respectively [18]. The  $\mu$ FCs in the best performance recollected 140 mW cm<sup>-2</sup>, and 0.51 V of power density and open circuit potential, using glucose dehydrogenase as the biocatalyst on single-walled carbon nanohorn. The present investigation collocated the perspective of using the biofuel cell as a portable power source.

Other researchers used soft drinks such as Nutri-Express, Coca Cola, and Minute Maid grape juice, as fuels in a miniature origami biofuel cell employed glucose dehydrogenase as bio-anode, obtaining power in the order of microwatts [19]. The system was described as a new approach for effective green energy systems.

In a third work [20], was reported a 3-cell stack paper-based biofuel cell powered by Gatorade<sup>(R)</sup> + NAD<sup>+1</sup> mM biofuel solutions at pH 7.3 (physiological pH). The anode (4.5 cm<sup>2</sup>) and the cathode (2.5 cm<sup>2</sup>) employed in this 3-cell stack were constructed employed Glucose Dehydrogenase (GDH) and Bilirubin oxidase (Box), respectively. The performance obtained through the stack system was from 1.8 V and 0.18 mWmg<sup>-1</sup> GDH (0.216 mW cm<sup>-2</sup>, calculated in this work from 3 mg GDH reported by the authors and cathode area).

Finally, in more recent research a miniature self-pumping paper-based enzymatic biofuel cell was constructed using glucose oxidase and laccase as anode and cathode, respectively, and soft drinks as fuels. The authors reported that power density obtained was attributed to the glucose contained in the soft drinks, which was fresh watermelon juice > 7up > Mountain Dew > Pepsi (14.5, 13.5, 12, and 6.15  $\mu$ Wcm<sup>-2</sup>) [21].

The above reports have used enzymatic electrodes for the oxidation of saccharides present in the soft drinks. As another alternative, the use of inorganic catalysts that oxidize saccharides in ideal and real conditions has been directed at the use of gold-based materials in many jobs [17,22–25].

In this sense, another material that has shown activity in the electro-oxidation of saccharides in fuel cells but has not had much application in real conditions has been the PtRu. This work has proposed a paper-based  $\mu$ FCs that use a catalyst anode such as PtRu/C, which is used due to a minimal poisoning rate and lower cost than Pt/C [26]. In addition, to assess their behavior, the individual voltammetry assessment of glucose, fructose, and maltose is reported, as well as the simulated Coca  $Cola^{(\mathbb{R})}$ , Pepsi<sup>(\mathbb{R})</sup>, Dr. Pepper<sup>(\mathbb{R})</sup>, and  $7up^{(\mathbb{R})}$ , evaluation, this means the mixture of these saccharides according to their reported content. Finally, the real soft drinks were employed, for the first time, like fuel in a non-enzymatic paper-based  $\mu$ FC; and the effect of two temperatures (4 °C, as consumption temperature and 25 °C, as room temperature) on the performance of the fuel cell was evaluated. The novelty of this work is the use of inorganic catalyst material in paper-based  $\mu$ FC for power generation using soft drinks as fuels. This approach has not been widely studied in this type of material. In addition, a new concept of emergency energy through this paper-based  $\mu$ FC was created. Furthermore, due to the easy access to sugary soft drinks that we have today, these paper microfluidic fuel cells could actually be applied as possible backup energy sources for low-consumption electronic devices. This article is outlined as follows: Section 2 depicts methodology, begins with the catalytic material used; Pt/C and Pt-Ru/C. After describing the electrochemical characterization to saccharides oxidation, in this section, describe so the design of the paper microfluidic fuel cell. Section 3 displays the results, and discussion about the characterization of Ru distribution on carbon paper, a cyclic voltammogram of PtRu/C in the presence of fructose, glucose, and maltose, after in presence on the  $\operatorname{Tup}^{\mathbb{R}}$ , Coca Cola<sup> $\mathbb{R}$ </sup>, Dr. Pepper<sup> $\mathbb{R}$ </sup>, and Pepsi<sup> $\mathbb{R}$ </sup>. Finally presents the polarization and power density curve.

## 2. Development of *µ*FC

## 2.1. Materials

All chemicals were reagent grade and were used without further modification. PtRu/C (20 wt.%) and Pt/C (30%) were from E-TEK. Nafion 5%, glucose, fructose, and maltose acquired from Sigma-Aldrich. Carbon paper Toray<sup>®</sup> was obtained from Technoquip Co Inc TGPH-120. Soft drinks were purchased from a local retail market. Isopropyl alcohol and KOH acquired from J.T. Baker. Whatman filter paper, grade Fusion 5 was used for paper-based  $\mu$ FC construction.

#### 2.2. PtRu/C Characterization

The experimental methodology started with the electrochemical characterization [23], of the catalytic properties of Pt/Ru for the saccharides (glucose, fructose, and maltose) oxidation. This electrochemical characterization consisted of cyclic voltammetry in a standard three-electrode glass cell using a saturated calomel electrode (SCE) and a Pt wire as reference electrode and counter electrode, respectively, and a glassy carbon electrode (3 mm diameter) modified with the PtRu/C ink as working electrode. All cyclic voltammetry experiments were conducted at 20 mVs<sup>-1</sup> and performed by potentiostat/galvanostat (Zahner Zennium). Half-cell studies consisted of four different conditions shown in Table 1. The conditions 1, 2, and 3 correspond to each concentration of the reported alone saccharides present in each soft drink [27] (glucose, fructose, and maltose) mixed in 20 mL of 0.3 M KOH. The condition 4 consisted of a mixture of all the previous saccharides inside each soft drink in 20 mL of 0.3 M KOH, obtaining a near simulated term. In all circumstances, the solutions were deoxygenated by N<sub>2</sub>-saturation (Infra, 99.999% pure) for 20 min at 25 °C.

To obtain a mapping of Ru was used as a HITACHI, Scanning Electron Microscope, Model SU 3500 & QUANTAX: Electron Dispersive Scattering for a Micro-analysis.

#### 2.3. Paper-Based Microfluidic Fuel Cell Assembly Process

After the evaluation of the electrocatalytic properties of PtRu, was proceeded to assembly the paper-based  $\mu$ FC. The electrodes consisted of a piece microporous carbon paper (Toray<sup>®</sup> Technoquip Co Inc TGPH-120) from 1.0 × 0.5 cm covered with a catalytic ink prepared using Nafion<sup>®</sup> 5% (Sigma-Aldrich), isopropyl alcohol (J.T. Baker) and PtRu/C (20 wt.% from E-TEK) or Pt/C (30 wt.% on Vulcan XC -72 from E-TEK) [9]. The ink over the electrodes was deposited using an airbrush,

and 1 mg cm<sup>-2</sup> metal loading was obtained. A foil of conducting aluminum was used to envelop the carbon paper electrodes as a contact.

Condition	Saccharide	$\begin{array}{c} \operatorname{Coca} \operatorname{Cola}^{(\!\overline{R})} \\ /\mathrm{mol} \ \mathrm{L}^{-1} \end{array}$	Pepsi <sup>®</sup> /mol L <sup>-1</sup>	Dr. Pepper <sup>®</sup> /mol L <sup>-1</sup>	7up <sup>®</sup> /mol L <sup>-1</sup>
1	Glucose	0.23	0.24	0.22	0.29
2	Fructose	0.35	0.36	0.34	0.25
3	Maltose	0.003		0.003	0.003
4	Glucose + Fructose + Maltose	Simulated Coca Cola	Simulated Pepsi	Simulated Dr. Pepper	Simulated 7up

Table 1. Half-cell conditions for soft drinks electro-oxidation on PtRu/C.

The paper-based  $\mu$ FC was made of an absorbent paper strip (whatman<sup>®</sup>, grade Fusion 5) composed with a fuel inlet of  $1.0 \times 0.3$  cm and a reaction zone of  $3.0 \times 0.7$  cm and delimited using a cutter plotter (Grapthec America Inc.) [9]. The schematic design of the paper-based  $\mu$ FC is presented in Figure 1. First, a rectangular size of  $5.0 \times 0.7$  cm of one layer of glass slide adhesive was cut with the objective of providing mechanical support to the paper-based  $\mu$ FC. On this adhesive layer was assembled the anode electrode; subsequently, the paper strip and cathode were collocated to form a sandwich structure. Placing the cathode on top facilitated oxygen access from the atmosphere.

On the other hand, for the construction of the 2-cell and 4-cell stacks, continuous pairs of electrodes were collocated (anode and cathode in the bottom and top, respectively) and rotated on the paper strip. Finally were connected following a serial connection using aluminum foil.



**Figure 1.** Components of fuel cell: (a) Schematic design of the paper-based microfluidic fuel cell and (b) dimension of the paper-based microfluidic fuel cell ( $\mu$ FC).

## 2.4. Performance of the Paper-Based Microfluidic Fuel Cell

In these experiments, the soft drinks were neither deoxygenated nor degassed. This condition could cause a bubble in the catalytic surface, causing an area in this surface without fuel, so the current and voltage could have a variation. This variation could cause unstable in the polarization curve. In all paper-based  $\mu$ FCs performance cases, the soft drinks were proved in two temperatures: at room temperature (27 °C) and cold (4 °C), this last temperature represents an adequate approximation of operation in a possible real application. Even though the soft drinks are available at a low cost

in large quantities, the paper-based  $\mu$ FCs present in this work is intended to be fed with a drop of soft drinks from the straw or with a small amount dropped of soft drink while the  $\mu$ FCs remains connected to some device, which limits the available volume of fuel significantly. For this reason, we standardized the volume of the experiments to 15  $\mu$ L, which is equivalent to the amount that could be present in a drop. Although the supply of soft drinks as fuel is not limited to this, for a possible real application. The resulting polarization and power density curves were recorded at 20 mVs<sup>-1</sup> using a Zahner Zennium potentiostat (PP211).

## 3. Results and Discussion

## 3.1. PtRu/C Characterization

The cyclic voltammograms (CVs) corresponding to the saccharides (glucose, fructose, and maltose) founded in all soft drinks used in this study ( $7up^{(R)}$ , Coca Cola<sup>(R)</sup>, Dr. Pepper<sup>(R)</sup>, and Pepsi<sup>(R)</sup>) showed similar behavior in all cases. In this sense, Figure 2 shows only the CVs in 0.3 M KOH on PtRu/C at a scan rate of 20 mVs<sup>-1</sup> in a potential range of -0.9 to 0.7 V for the concentration of the saccharide in  $7up^{(R)}$ .



**Figure 2.** Cyclic voltammograms of PtRu/C on a glassy carbon electrode in the presence of fructose, glucose, and maltose in 0.3 M KOH, the scan rate of 20 mVs<sup>-1</sup> at room temperature at the concentration corresponding to  $7up^{(R)}$ .

Three peaks at -0.63, -0.10, and 0.57 V in the forward scan were observed for the glucose oxidation test (blue line in Figure 2). The peak at -0.63 V originated due to dehydrogenation of glucose (Figure 3a) in the hydrogen wave region; this peak was observed for fructose too at -0.55 V (black line in Figures 2 and 3b). The peaks at -0.10 and -0.14 V for glucose oxidation and fructose oxidation, respectively emerged at the potential region where the electrode surface is partially covered by adsorbed OH<sup>-</sup>. In this region, the adsorbed OH<sup>-</sup> on catalyst surface can oxidize glucose and fructose directly. The peak at 0.57 V was observed due to oxidation of the platinum surface [26,28–32]. For maltose oxidation, peak at -0.70 V in a forward scan was observed due to the oxidation of maltose to D-maltbionic acid (red line in Figures 2 and 3c) [33].

On the other hand, Figure 4 shows the cyclic voltammograms corresponding to simulated soft drinks, which are composed of the same concentrations of saccharides present in each soft drink as, shown in Table 1, but in this case, all are homogeneously dissolved in a 0.3 M KOH solution. In all cases, saccharide oxidation reaction curves are observed in PtRu/C at 20 mVs<sup>-1</sup> in a potential range of -0.9 to 0.7 V.



Figure 3. Oxidation reactions of saccharides: (a) glucose, (b) fructose, and (c) maltose.



**Figure 4.** Cyclic voltammograms of PtRu/C on glassy carbon electrode in presence of simulated  $7up^{(R)}$ , Coca Cola<sup>(R)</sup>, Dr. Pepper<sup>(R)</sup>, and Pepsi<sup>(R)</sup> at a scan rate of 20 mVs<sup>-1</sup> at room temperature.

The forms of the voltammograms were very similar between them and are characterized by the presence of three peaks in the forward scans. It is interesting that the position of the peaks for the simulated drinks, they very close to the position of the glucose oxidation peaks in PtRu/C found previously (Figure 2). Therefore the distribution of Ru it shows in Figure 5, and glucose oxidation is predominant on PtRu/C despite the presence of the other saccharides [31], and [34,35] used in this study.



Figure 5. Fuel cell and material catalytic: (a) mapping of Ru, (b) micro-fuel cell photography.

These tests show an approach to check the oxidation of saccharides via electrochemistry, leaving as a basis for the possible use of soft drinks as a source of saccharides.

#### 3.2. Soft Drinks Paper-Based Microfluidic Fuel Cell Performance

Figure 6 shows the polarization and power density curves for each paper-based microfluidic fuel cell operated with 7up<sup>®</sup>, Coca Cola<sup>®</sup>, Dr. Pepper<sup>®</sup>, and Pepsi<sup>®</sup> as an energy source, respectively, at room temperature (27 °C) and cold (4 °C). Table 2 shows the experimental parameters obtained from the overall performance of the paper-based  $\mu$ FCs with the different soft drinks as fuels. From Figure 6, can be seen that the fuels that offer the best performance are 7up<sup>®</sup>, Coca Cola<sup>®</sup>, Dr. Pepper<sup>®</sup> in that order which yields maximum power densities of 0.073, 0.063, 0.061, and 0.060 mW cm<sup>-2</sup> and 0.120, 0.113, 0.112, and 0.111 mW cm<sup>-2</sup>, for room and cold temperature, respectively. These results have been resumed in Table 2, and confirm that glucose oxidation is predominant on PtRu/C in the presence of fructose and maltose since the order of the performance of the devices coincides with the order of the concentration of glucose in each soft drink, which is 7up<sup>®</sup> > Pepsi<sup>®</sup> > Coca Cola<sup>®</sup> > Dr. Pepper<sup>®</sup>.

Soft Drink	OCP /V	J /mA cm <sup>-2</sup>	P MAX /mW cm <sup>-2</sup>
Coca Cola $^{(\!\!\!\!R)}$ at room temperature	$0.63\pm0.09$	$0.43\pm0.03$	$0.061\pm0.004$
Cold Coca Cola <sup>®</sup>	$0.60\pm0.08$	$0.75\pm0.06$	$0.112\pm0.008$
Pepsi <sup>®</sup> at room temperature	$0.55\pm0.06$	$0.34\pm0.03$	$0.063\pm0.003$
Cold Pepsi <sup>®</sup>	$0.62\pm0.07$	$0.64\pm0.05$	$0.113\pm0.007$
Dr. Pepper <sup>(<math>\mathbb{R}</math>)</sup> at room temperature	$0.64\pm0.08$	$0.45\pm0.04$	$0.060\pm0.004$
Cold Dr. Pepper <sup>®</sup>	$0.67\pm0.07$	$0.67\pm0.05$	$0.111\pm0.007$
$7up^{\textcircled{R}}$ at room temperature	$0.69\pm0.06$	$0.37\pm0.03$	$0.073\pm0.005$
Cold 7up <sup>(R)</sup>	$0.64\pm0.05$	$0.62\pm0.05$	$0.120\pm0.007$

**Table 2.** Experimental parameters obtained from the overall performance of the paper-based  $\mu$ FCs with different soft drinks as fuels. Results are expressed as mean values (n = 3) ± standard deviation.

In all cases, the power density values show an increase for each cold soft drink in comparison with room temperature, suggesting that the temperature plays an essential role for the improved electro-catalytic performance of the device, as is known, the operation of these devices is limited by the  $O_2$  reduction reaction that exists in the cathode according to Equation (1), despite the use of Pt, which is the best catalyst for this reaction and taking into account that the way in which the reaction occurs is highly influenced by the surface on which it is given, in addition to the conditions of the reaction medium [36–38].

$$O_2 + 4H^+ + 4^{e^-} \to 2H_2O$$
  $E^0 = 1.229 V$  (1)



**Figure 6.** Polarization and power density curves of PtRu/C and Pt/C as anode and cathode, respectively that uses real soft drink cold (solid Figures) and soft drink at room temperature (open Figures) as fuel and air as oxidant. (a)  $\operatorname{Pup}^{\mathbb{R}}$ , (b) Coca Cola<sup> $\mathbb{R}$ </sup>, (c) Dr. Pepper<sup> $\mathbb{R}$ </sup>, and (d) Pepsi<sup> $\mathbb{R}$ </sup>.

Despite its high spontaneity, the problem with oxygen reduction lies in a large amount of energy that must be supplied to the molecule for the activation of the double bond ( $498 \text{ kJ mol}^{-1}$ ), which makes this reaction kinetically impeded [38]. Kinetically, it is ideal that the reaction occurs as close as possible to the thermodynamic reaction potential [39], with a high reaction speed, or at least sufficient for the needs of each case. The current-overpotential relationship is given by the Butler–Volmer equation (Equation (2)).

$$i_c = i^0 \left( e^{\frac{n\alpha F \eta_c}{RT}} \right) - e^{\frac{n(\alpha - 1)F \eta_c}{RT}}$$
(2)

where  $i_c$  is the current density of the oxygen reduction reaction,  $i^0$  is the current exchange density, n is the number of electrons transferred in the step that determines the reaction rate,  $\alpha$  is the transfer coefficient,  $\eta_c$  is the overpotential for the oxygen reduction reaction, F is Faraday's constant, R the constant of the ideal gases, and T the temperature in Kelvin degrees. For the current density of the reaction to be high to on low overpotentials, it must be fulfilled that, the exchange current ( $i^0$ ) be high, or the factor  $\alpha F(RT)^{-1}$  be big. A decrease in temperature would cause an increase in this factor, considering that the other parameters do not change because the same surface is used as a catalyst and the same medium, increasing the contribution of the oxygen reduction reaction current and, therefore, the performance of the cell.

The power density obtained when each soft drink is used as fuel is a maximum advance from the economic and environmental standpoints; it is possible to obtain power densities using a cheaper,

common, and easily available soft drink as fuel. It is important to note that these soft drinks are less expensive than other fuel commonly used in paper-based  $\mu$ FCs, because the soft drink does not need preparation in the laboratory. Figure 7, shows the development of the open circuit potential (OCP), for a paper-based  $\mu$ FCs for cases 7up<sup>®</sup>, Coca Cola<sup>®</sup>, Dr. Pepper<sup>®</sup>, and Pepsi<sup>®</sup>.



**Figure 7.** Open circuit potential stability, for a paper-based  $\mu$ FCs for cases  $7up^{(\mathbb{R})}$ , Coca Cola<sup>(\mathbb{R})</sup>, Dr. Pepper<sup>(\mathbb{R})</sup>, and Pepsi<sup>(\mathbb{R})</sup>.

These tests (Figure 7) evaluated the capabilities of the paper-based  $\mu$ FC to recover after three cycles of charging/discharging its open circuit potential. The time required for this test was determined based on the drying of 15  $\mu$ L of soft drink (10 to 15 min). The charge–discharge experiments using OCP refer to the following: first, the OCP is measured vs. time until it reaches its maximum value (stability), then a discharge curve is realized (voltage vs. current) until the voltage reaches zero. After that, the recovery of the OCP vs. time is measured again; this process is done three times. In this way, we analyze the OCP obtain after each cycle of charge/discharge. It can observe an increase in potential as soon as the fuel comes into contact with the electrodes showing that the oxidation reaction of the glucose is taking place. In addition, the potential is stabilized at 700, 670, 650, and 640 mV for 7up<sup>®</sup>, Dr. Pepper<sup>®</sup>, Pepsi<sup>®</sup>, and Coca Cola<sup>®</sup>, respectively. During the charging period, the potential tends to return to the initial value at which it stabilized and remains constant as time passes and with each cycle. These results indicate that the devices are quite stable after charging/discharging cycles so that only one of them could be occupied in a successive manner for the generation of electricity using soft drinks as fuel.

For comparative purposes, Table 3 shows the results obtained in different reports in which they have used soft drinks as fuel and this work. It is seen that the obtained maximum values are within the range of those already reported for these fuels. However, this work offers the advantage of the use of devices that do not use enzymatic anodes, so the lifetime of the paper-based  $\mu$ FCs is bigger, and the cost of generating electricity would be much lower.

## 3.3. Soft-Drinks Paper-Based Microfluidic Fuel Cell Performance Stack as a Possible Backup Power Supply

The 2-cell and 4-cell stacks were developed and demonstrated the usefulness of the paper-based  $\mu$ FCs as a backup possible power supply. The polarization and power density curves for each fuel cell-stack operated with Coca Cola<sup>®</sup> as fuel are showed in Figure 8. Coca Cola<sup>®</sup> was chosen as fuel for this test because it is one of the most consumed soft drinks in the world, so it would have a higher chance of being used in a real application.

Soft Drink	Fuel Cell Type	OCP /V	PMAX /mW cm <sup>-2</sup>	Reference
Vegetable juice	Miniature glucose/air biofuel cell	0.71	0.245	[18]
Nutri-Express	Miniature origami biofuel cell	0.3	$\approx 0.008$	[19]
Coca Cola	Miniature origami biofuel cell	$\approx 0.09$	$\approx 0.0006$	[19]
Gatorade	3-cell stack paper based biofuel cell	1.8	0.216	[20]
7up	Miniature self-pumping paper-based enzymatic biofuel cell	0.31	0.0135	[21]
Mountain Dew	Miniature self-pumping paper-based enzymatic biofuel cell	0.39	0.012	[21]
Pepsi	Miniature self-pumping paper-based enzymatic biofuel cell	0.32	0.00615	[21]
Coca Cola at room temperature	Paper-based microfluidic fuel cell	0.6	0.061	This work
Cold 7up	Paper-based microfluidic fuel cell	0.64	0.12	This work
Cold Com Colo	2 and 4-cell stack paper-based microfluidic fuel cell		0.27	This work
Cold Coca-Cola			0.39	This work

An increase in open circuit potential and maximum power density was found when a serial connection for 2 and 4 paper-based  $\mu$ FC (1.07, 1.6 V and 0.27, 0.4 mW cm<sup>-2</sup>, respectively) was realized respect to a single a paper-based  $\mu$ FC (0.6 V). However, according to the Kirchhoff's voltage law, an optimal doubling and quadrupling of the 2-cell and 4-cell performance were expected; nevertheless, this was not found due losses associated with the resistance imposed by the electric circuit used in the stack and some contact deficiencies of the electrodes with the conductor wires because its small size makes it difficult to handle.



**Figure 8.** Polarization and power density curves of PtRu/C and Pt/C as anode and cathode, respectively in 2- and 4-cell paper-based microfluidic stacks using Coca Cola<sup> $\mathbb{R}$ </sup> as fuel and air as oxidant.

# 4. Conclusions

In this work, the soft drinks have been used as an energy source in paper-based  $\mu$ FCs. In addition, the use of cold soft drinks showed a better performance than soft drinks at room temperature. However, in a possible real application, the temperature would increase as a function of time, causing a decrease in the performance of the fuel cell. The study of this decrease in performance with respect to temperature could be of interest for future research. On the other hand, the material used (commercial PtRu/C) as a catalyst for the oxidation of the saccharides showed that glucose oxidation is predominant in the presence of maltose and fructose so that the performance of the devices was directly affected by the glucose concentration. We foresee that combining the advantages in the materials field to use other

catalysts on the paper-based  $\mu$ FCs would lead to better performances. The design of the presented paper-based  $\mu$ FC has been inspired in a single flow. In this sense, the study of the flow velocity induced by capillary action respect to the configuration of the fuel cell could simulate through software such as ANSYS. The use of different soft drinks as energy sources represents a great contribution to the field of fuel cells due to the price, availability, and environmentally friendly of these beverages. This suggests that the use of soft drinks as fuels in paper-based  $\mu$ FCs constitutes a hopeful alternative for small portable electronic devices. In addition, the use of other easily accessible fuels could be considered.

Author Contributions: Conceptualization, J.H.R. and D.D.; methodology, H.E.E.P.; validation, J.M.O.R., A.D.; and J.R.-R.; formal analysis, D.O.D.; investigation, R.G.; resources, D.M.A.C. All authors have read and agreed to the published version of the manuscript

**Funding:** The authors appreciate the founding of CONACyT for "Cátedras CONACyT" project 513 and PRODEP. **Acknowledgments:** The authors gratefully acknowledge to UAQ, UTSJR, SEP and CONACyT.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

- 1. Xie, L.; Li, J.; Cai, S.; Li, X. Design and experiments of a self-charged power bank by harvesting sustainable human motion. *Adv. Mech. Eng.* **2016**, *8*, 1687814016651371. [CrossRef]
- 2. Alanís-Navarro, J.; Reyes-Betanzo, C.; Moreira, J.; Sebastian, P. Fabrication and characterization of a micro-fuel cell made of metallized PMMA. *J. Power Sources* **2013**, 242, 1–6. [CrossRef]
- Esquivel, J.; Senn, T.; Hernández-Fernández, P.; Santander, J.; Lörgen, M.; Rojas, S.; Löchel, B.; Cané, C.; Sabaté, N. Towards a compact SU-8 micro-direct methanol fuel cell. *J. Power Sources* 2010, 195, 8110–8115. [CrossRef]
- 4. Moreno-Zuria, A.; Dector, A.; Cuevas-Muñiz, F.; Esquivel, J.; Sabaté, N.; Ledesma-García, J.; Arriaga, L.; Chávez-Ramírez, A. Direct formic acid microfluidic fuel cell design and performance evolution. *J. Power Sources* **2014**, *269*, 783–788. [CrossRef]
- 5. Hashemi, S.; Neuenschwander, M.; Hadikhani, P.; Modestino, M.; Psaltis, D. Membrane-less micro fuel cell based on two-phase flow. *J. Power Sources* **2017**, *348*, 212–218. [CrossRef]
- 6. Morales-Acosta, D.; Godinez, L.A.; Arriaga, L. Performance increase of microfluidic formic acid fuel cell using Pd/MWCNTs as catalyst. *J. Power Sources* **2010**, *195*, 1862–1865. [CrossRef]
- 7. Esquivel, J.; Del Campo, F.; De La Fuente, J.G.; Rojas, S.; Sabate, N. Microfluidic fuel cells on paper: meeting the power needs of next generation lateral flow devices. *Energy Environ. Sci.* **2014**, *7*, 1744–1749. [CrossRef]
- González-Guerrero, M.J.; Del Campo, F.J.; Esquivel, J.P.; Leech, D.; Sabaté, N. based microfluidic biofuel cell operating under glucose concentrations within physiological range. *Biosens. Bioelectron.* 2017, 90, 475–480. [CrossRef]
- Dector, A.; Galindo-De-La-Rosa, J.; Amaya-Cruz, D.; Ortíz-Verdín, A.; Guerra-Balcázar, M.; Olivares-Ramírez, J.; Arriaga, L.; Ledesma-García, J. Towards autonomous lateral flow assays: Paper-based microfluidic fuel cell inside an HIV-test using a blood sample as fuel. *Int. J. Hydrogen Energy* 2017, 42, 27979–27986. [CrossRef]
- Kjeang, E.; Djilali, N.; Sinton, D. Microfluidic fuel cells: A review. J. Power Sources 2009, 186, 353–369. [CrossRef]
- Lau, C.; Moehlenbrock, M.J.; Arechederra, R.L.; Falase, A.; Garcia, K.; Rincon, R.; Minteer, S.D.; Banta, S.; Gupta, G.; Babanova, S.; et al. Paper based biofuel cells: Incorporating enzymatic cascades for ethanol and methanol oxidation. *Int. J. Hydrogen Energy* 2015, 40, 14661–14666. [CrossRef]
- Copenhaver, T.S.; Purohit, K.H.; Domalaon, K.; Pham, L.; Burgess, B.J.; Manorothkul, N.; Galvan, V.; Sotez, S.; Gomez, F.A.; Haan, J.L. A microfluidic direct formate fuel cell on paper. *Electrophoresis* 2015, *36*, 1825–1829. [CrossRef]
- 13. Chino, I.; Muneeb, O.; Do, E.; Ho, V.; Haan, J.L. A paper microfluidic fuel cell powered by urea. *J. Power Sources* **2018**, *396*, 710–714. [CrossRef]
- 14. Castillo-Martínez, L.; Amaya-Cruz, D.; Gachuz, J.; Ortega-Díaz, D.; Olivares-Ramírez, J.; Dector, D.; Duarte-Moller, A.; Villa, A.; Dector, A. Urea oxidation in a paper-based microfluidic fuel cell using Escherichia coli anode electrode. *J. Phys. Conf. Ser.* **2018**, *1119*, 012004. [CrossRef]

- González-Guerrero, M.J.; del Campo, F.J.; Esquivel, J.P.; Giroud, F.; Minteer, S.D.; Sabaté, N. based enzymatic microfluidic fuel cell: From a two-stream flow device to a single-stream lateral flow strip. *J. Power Sources* 2016, 326, 410–416. [CrossRef]
- 16. Shyu, J.C.; Wang, P.Y.; Lee, C.L.; Chang, S.C.; Sheu, T.S.; Kuo, C.H.; Huang, K.L.; Yang, Z.Y. Fabrication and test of an air-breathing microfluidic fuel cell. *Energies* **2015**, *8*, 2082–2096. [CrossRef]
- Dector, D.; Olivares-Ramírez, J.; Ovando-Medina, V.; Dominguez, A.S.; Villa, A.; Duarte-Moller, A.; Sabaté, N.; Esquivel, J.; Dector, A. Fabrication and evaluation of a passive SU8-based micro direct glucose fuel cell. *Microsyst. Technol.* 2019, 25, 211–216. [CrossRef]
- 18. Wen, D.; Xu, X.; Dong, S. A single-walled carbon nanohorn-based miniature glucose/air biofuel cell for harvesting energy from soft drinks. *Energy Environ. Sci.* **2011**, *4*, 1358–1363. [CrossRef]
- 19. Yu, Y.; Han, Y.; Lou, B.; Zhang, L.; Han, L.; Dong, S. A miniature origami biofuel cell based on a consumed cathode. *Chem. Commun.* **2016**, *52*, 13499–13502. [CrossRef]
- 20. Villarrubia, C.W.N.; Lau, C.; Ciniciato, G.P.; Garcia, S.O.; Sibbett, S.S.; Petsev, D.N.; Babanova, S.; Gupta, G.; Atanassov, P. Practical electricity generation from a paper based biofuel cell powered by glucose in ubiquitous liquids. *Electrochem. Commun.* **2014**, *45*, 44–47. [CrossRef]
- 21. Rewatkar, P.; Goel, S. Microfluidic paper based membraneless biofuel cell to harvest energy from various beverages. *J. Electrochem. Sci. Eng.* **2020**, *10*, 49–54. [CrossRef]
- 22. Dector, A.; Arjona, N.; Guerra-Balcázar, M.; Esquivel, J.; Campo, F.D.; Sabaté, N.; Ledesma-García, J.; Arriaga, L. Non-Conventional Electrochemical Techniques for Assembly of Electrodes on Glassy Carbon-Like PPF Materials and Their Use in a Glucose Microfluidic Fuel-Cell. *Fuel Cells* **2014**, *14*, 810–817. [CrossRef]
- López Zavala, M.Á.; González Peña, O.I.; Cabral Ruelas, H.; Delgado Mena, C.; Guizani, M. Use of Cyclic Voltammetry to Describe the Electrochemical Behavior of a Dual-Chamber Microbial Fuel Cell. *Energies* 2019, 12, 3532. [CrossRef]
- Olivares-Ramírez, J.; Ovando-Medina, V.; Ortíz-Verdín, A.; Amaya-Cruz, D.; Coronel-Hernandez, J.; Marroquín, A.; Dector, A. Lateral flow assay HIV-based microfluidic blood fuel cell. *J. Phys. Conf. Ser.* 2018, 1119, 012022. [CrossRef]
- 25. Ovando-Medina, V.; Dector, A.; Antonio-Carmona, I.; Romero-Galarza, A.; Martínez-Gutiérrez, H.; Olivares-Ramírez, J. A new type of air-breathing photo-microfluidic fuel cell based on ZnO/Au using human blood as energy source. *Int. J. Hydrogen Energy* **2019**, *44*, 31423–31433. [CrossRef]
- 26. Basu, D.; Basu, S. Synthesis, characterization and application of platinum based bi-metallic catalysts for direct glucose alkaline fuel cell. *Electrochim. Acta* **2011**, *56*, 6106–6113. [CrossRef]
- 27. Walker, R.W.; Dumke, K.A.; Goran, M.I. Fructose content in popular beverages made with and without high-fructose corn syrup. *Nutrition* **2014**, *30*, 928–935. [CrossRef]
- 28. Haynes, T.; Dubois, V.; Hermans, S. Particle size effect in glucose oxidation with Pd/CB catalysts. *Appl. Catal. A Gen.* **2017**, *542*, 47–54. [CrossRef]
- 29. Amani-Beni, Z.; Nezamzadeh-Ejhieh, A. NiO nanoparticles modified carbon paste electrode as a novel sulfasalazine sensor. *Anal. Chim. Acta* **2018**, *1031*, 47–59. [CrossRef]
- 30. Ibrahim, A.A.; Umar, A.; Amine, A.; Kumar, R.; Al-Assiri, M.; Al-Salami, A.; Baskoutas, S. Highly sensitive and selective non-enzymatic monosaccharide and disaccharide sugar sensing based on carbon paste electrodes modified with perforated NiO nanosheets. *New J. Chem.* **2018**, *42*, 964–973. [CrossRef]
- Mahshid, S.S.; Mahshid, S.; Dolati, A.; Ghorbani, M.; Yang, L.; Luo, S.; Cai, Q. Template-based electrodeposition of Pt/Ni nanowires and its catalytic activity towards glucose oxidation. *Electrochim. Acta* 2011, *58*, 551–555. [CrossRef]
- 32. Basu, D.; Basu, S. A study on direct glucose and fructose alkaline fuel cell. *Electrochim. Acta* **2010**, *55*, 5775–5779. [CrossRef]
- 33. Morrison, R.; Boyd, R. Organic Chemistry, 5th ed.; Allyn and Bacon: Boston, MA, USA, 1987.
- 34. Tao, B.; Zhao, K.; Miao, F.; Jin, Z.; Yu, J.; Chu, P.K. Fabrication of ordered porous silicon nanowires electrode modified with palladium-nickel nanoparticles and electrochemical characteristics in direct alkaline fuel cell of carbohydrates. *Ionics* **2016**, *22*, 1891–1898. [CrossRef]
- 35. Liu, X.; Long, L.; Yang, W.; Chen, L.; Jia, J. Facilely electrodeposited coral-like copper micro-/nano-structure arrays with excellent performance in glucose sensing. *Sens. Actuators B Chem.* **2018**, 266, 853–860. [CrossRef]
- 36. Perez, J.; Villullas, H.M.; Gonzalez, E.R. Structure sensitivity of oxygen reduction on platinum single crystal electrodes in acid solutions. *J. Electroanal. Chem.* **1997**, *435*, 179–187. [CrossRef]

- 37. Su, F.; Poh, C.K.; Tian, Z.; Xu, G.; Koh, G.; Wang, Z.; Liu, Z.; Lin, J. Electrochemical behavior of Pt nanoparticles supported on meso-and microporous carbons for fuel cells. *Energy Fuels* **2010**, *24*, 3727–3732. [CrossRef]
- 38. Hsueh, K.; Gonzalez, E.; Srinivasan, S. Electrolyte effects on oxygen reduction kinetics at platinum: A rotating ring-disc electrode analysis. *Electrochim. Acta* **1983**, *28*, 691–697. [CrossRef]
- 39. Gewirth, A.A.; Thorum, M.S. Electroreduction of dioxygen for fuel-cell applications: Materials and challenges. *Inorg. Chem.* **2010**, *49*, 3557–3566. [CrossRef]



 $\odot$  2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).